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THEORETICAL PREDICTION
OF VIBRATIONAL CIRCULAR DICHROISM SPECTRA

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PREFACE

The work described in this report was authorized under Project No. 1L162622A553I, CB Simulants, Survivability, and System Science, Project No. 1C464806D020, Chemical Detection, Identification and Warning, and Contract No. DAAL03-86-D-001. This work was started in June 1989 and completed in September 1989.

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THEORETICAL PREDICTION OF VIBRATIONAL CIRCULAR DICHROISM SPECTRA

1. INTRODUCTION

A requirement for this study was the interest of the Detection Group at CRDEC in being able to detect biological materials in the field. A reasonable means to this objective is through the recognition that sugars are distinguishing features of biological materials. Sugars are optically active and can be studied through a variety of techniques. The technique of interest here is vibrational circular dichroism (VCD). The predicted VCD spectra can also be related to the (1,4) matrix element of the Mueller matrix, to be discussed in section II. A procedure to obtain all of 16 elements of the (4x4) Mueller matrix simultaneously by a two laser spectroscopic measurement is presently being implemented by one of the authors (AHC). The calculated spectra of sugars, at a minimum, should assist laboratory measurements on sugars. The practical questions as to whether real biological materials can be detected and the limits of detectability await future experimental studies. Because the techniques of computational chemistry are now cheaper and faster than extensive experimental techniques, quantum chemistry is employed to identify spectral regions of interest and what compounds can be detected by VCD. Furthermore, a library can be constructed that will permit matching of experimental results to unambiguously identify unknown compounds. This report will focus on the application of current computational techniques to the study of sugars, sugar-like molecules and other molecules of interest. This study can be viewed as the beginning phase of the generation of a library of theoretically predicted VCD spectra.

This report is organized in the following sections: section II is a background section on VCD in general, the Stephens' formulation (1,2) of the rotational strength of a vibrational transition and the concept of a Mueller matrix; section III focusses on three classes of molecules that were investigated; section IV discusses the work suggested for continuation of this study; section V summarizes the report.

2. BACKGROUND

2.1 *Vibrational Circular Dichroism*

Molecules that interact differently with left circularly polarized (LCP) and right circularly polarized (RCP) radiation are optically active. Two phenomena linked to optical activity are:

- (1) optical rotation
- (2) circular dichroism

Optical rotation involves the rotation of a plane of linearly polarized radiation as it is passed through a sample. Circular dichroism is the difference in the absorption of LCP and RCP radiation by a sample. In the absence of applied fields, optical activity arises from chirality, which exists when a molecule is not superimposable on its mirror image - i.e. a molecule must not possess any elements of symmetry to be optically active.

In the early 1970's instrumentation was devised to measure the VCD spectrum of a chiral molecule. Here, the difference in absorptivity of a sample between LCP and RCP radiation is plotted as a function of wavenumber. A typical VCD spectrum is shown in Figure 1. Figure 1 includes both the VCD spectrum of methyl thiirane over the wavenumber range of 1500-800 cm^{-1} and the IR

spectrum for the purpose of comparison. As can be noted the rotational strengths, i.e. the difference in absorptivity of a sample between LCP and RCP radiation, can be positive or negative and the intensities are not related to the infrared and Raman intensities. The essential points to be studied in this investigation are frequencies, magnitudes of intensities and signs of intensities. All notations used in the following sections are consistent with those of Stephens (1,2).

2.2 Stephens' Formulation of the Rotational Strength

P. J. Stephens (1,2) has developed a theory for the determination of the rotational strength of a vibrational transition $g \rightarrow e$, $R(g \rightarrow e)$, for a chiral molecule;

$$R(g \rightarrow e) = \sum_{\beta} \text{Im}[\langle g | (\mu_d)_{\beta} | e \rangle \langle e | (\mu_{mag})_{\beta} | g \rangle] \quad [\beta = x, y, z] \quad (1)$$

where g and e are ground and excited states and μ_e and μ_{mag} are electric and magnetic dipole moment operators. For a given fundamental vibrational mode of frequency ω_i , the electric and magnetic dipole transition moments for the $0 \rightarrow 1$ vibrational transition is given by;

$$\langle 0 | (\mu_d)_{\beta} | 1 \rangle_i = (h/2\omega_i)^{1/2} \sum_{\lambda\alpha} P_{\alpha\beta}^{\lambda} S_{\lambda\alpha,i} \quad (2)$$

$$\langle 0 | (\mu_{mag})_{\beta} | 1 \rangle_i = -(2h^3\omega_i)^{1/2} \sum_{\lambda\alpha} M_{\alpha\beta}^{\lambda} S_{\lambda\alpha,i} \quad (3)$$

$P_{\alpha\beta}^{\lambda}$ and $M_{\alpha\beta}^{\lambda}$ are atomic polar and atomic axial tensors defined by

$$P_{\alpha\beta}^{\lambda} = E_{\alpha\beta}^{\lambda} + N_{\alpha\beta}^{\lambda} \quad (4)$$

$$M_{\alpha\beta}^{\lambda} = I_{\alpha\beta}^{\lambda} + J_{\alpha\beta}^{\lambda} \quad (5)$$

$$E_{\alpha\beta}^{\lambda} = [(\partial/\partial X_{\lambda\alpha}) \langle \psi_d(\vec{R}) | (\mu_d)_{\beta} | \psi_d(\vec{R}) \rangle]_{\vec{R}_0} \quad (6)$$

$$N_{\alpha\beta}^{\lambda} = Z_{\lambda} e \delta_{\alpha\beta} \quad (7)$$

$$I_{\alpha\beta}^{\lambda} = \langle (\partial \psi_d(\vec{R}) / \partial X_{\lambda\alpha})_{\vec{R}_0} | (\partial \psi_d(\vec{R}) / \partial H_{\beta})_{H_{\beta}=0} \rangle \quad (8)$$

$$J_{\alpha\beta}^{\lambda} = (i/4hc) \sum_{\gamma} \epsilon_{\alpha\beta\gamma} (Z_{\lambda} e) R_{\lambda\gamma}^{\circ} \quad (9)$$

where

\vec{R}	=	the nuclear geometry
\vec{R}_0	=	the equilibrium nuclear geometry
$X_{\lambda\alpha}$	=	cartesian displacement coordinates ($\alpha = x, y, z$) from equilibrium of nucleus λ
$Z_{\lambda} e$	=	charge on nucleus λ

\bar{R}_λ^0	=	equilibrium position of nucleus λ
G	=	electronic ground state
μ_{ei}^e	=	electronic contribution to μ_{ei}
$\psi_G(\bar{R}_0, H_p)$	=	electronic wavefunction of G at \bar{R}_0 in the presence of the perturbation $H = -(\mu_{mag}^e)_p H_p$
$\epsilon_{\alpha\beta\gamma}$	=	antisymmetric unit third rank tensor

Note that;

$$X_{\lambda\alpha} = \sum_i S_{\lambda\alpha i} Q_i$$

i.e. $S_{\lambda\alpha i}$ is a matrix element in the transformation between the cartesian coordinates and the normal coordinates.

2.3 Mueller Matrix

Let us now turn to a brief discussion of the definition and use of a Mueller matrix. First let us consider the transmission of electromagnetic radiation. The interaction of polarized radiation with an optical element (polarizer, retarder, reflector, scatterer) can be described by specifying the polarization state of incident and transmitted radiation. A typical experimental setup is shown in Figure 2. One convenient description of the radiation involves use of Stokes vectors and the use of a transformation between the transmitted radiation, σ_t , and the incident radiation σ_i which is termed the Mueller matrix (3,4), T

$$\sigma_t = T \sigma_i \quad (10)$$

All of the information concerning the transmission of radiation by an optical element is contained in the 16 elements of the transformation Mueller matrix. The Stokes parameters, components of a Stokes vector are defined by

$$I = \langle E E^* + E E^* \rangle \quad (11)$$

$$Q = \langle E E^* - E E^* \rangle \quad (12)$$

$$U = \langle E E^* + E E^* \rangle \quad (13)$$

$$V = i \langle E E^* - E E^* \rangle \quad (14)$$

where the angular brackets indicates a time average over an interval long compared with the period of a quasi-monochromatic beam described by an electric field E with orthogonal axes perpendicular to the direction of propagation. Typical Stokes vectors are shown in Table 1.

Now if scattered radiation from a single particle or a collection of particles is studied as shown in Figure 3 an analogous Mueller matrix for scattering (5), S, can be setup

$$\sigma_s = S\sigma_i \quad (15)$$

where

$$\begin{aligned} \sigma_s &= \text{Stokes Vector for scattered light} \\ \sigma_i &= \text{Stokes Vector for incident light} \end{aligned}$$

If the incident light is right-circularly polarized, then the irradiance I_R of the scattered light is related to $S_{11} + S_{14}$. Also, the irradiance I_L of the scattered light is related to $S_{11} - S_{14}$. The Mueller scattering matrix element S_{14} can be expressed as

$$S_{14} = (I_R - I_L) / 2I_i \quad (16)$$

where I_i is the intensity of the incident light. The matrix element S_{14} is readily interpretable in terms of the difference of the irradiances of scattered light for incident right-circularly and left-circularly polarized light. In this case the VCD intensity is directly proportional to the S_{14} matrix element. As a result a VCD theoretical spectrum can be used to predict the magnitude of the Mueller matrix element S_{14} .

3. RESULTS

The Chemometric and Biometric Modeling Branch (CBM) of CRDEC has undertaken the task of generating a library of theoretically determined VCD spectra for sugars, sugar-like molecules and other molecules of interest. The calculations have proceeded in the following stepwise manner:

1. the software package MMADS (6) was run using the option MODEL in order to obtain a crude geometry
2. the structure obtained in step (1) was then optimized using MOPAC version 3.0 (7)
3. optimized structures using the Gaussian programs Gaussian 82 (8-11) or CADPAC version 4.0 (12) were obtained. (Both packages yield identical results both in terms of total energy and optimized structure.)
4. frequencies and rotational strengths were obtained by running CADPAC version 4.0 (12) on a CRAY-XMP computer.

The calculations at this point have been largely carried out at the 3-21G level. This level was selected because past experience indicates very reasonable optimized structures are found as compared to experimental structures. As is well known with ab initio determination of vibrational motion, the vibrational frequencies are typically too high - e.g. the C-H stretch predicted for 3-21 G level calculations multiplied by a scaling factor of 0.89, found empirically, is in very good agreement with experimental data (13).

Attention has been focussed on the following areas:

1. determination of the VCD spectrum for molecules for which literature results are available - the molecules selected here are ethylene oxide (14), the isotopically substituted ammonia molecule (NHDT) (15,16), and methyl thiirane (17-19).
2. prediction of VCD spectra for other molecules of interest - hydrogen peroxide, HOOH, and hydrogen persulfide, HSSH.
3. prediction of VCD spectral parameters for molecules that have functionalities similar to sugars (hydroxyacetaldehyde, hydroxymethyl ether, ethylene glycol and dimethyl ether) and sugars with 3 carbon atoms (D-glyceraldehyde) and 4 carbon atoms (D-erythrose, and D-threose).

Our objectives are the following:

1. develop the VCD parameters (frequency and rotational strengths) in the range 800-1200 cm^{-1} that indicate transitions of high rotational strength and predict the correct sign.
2. develop the VCD parameters as accurately as possible, within a procedure that is computationally reasonable, for sugars in order that the results can be dovetailed into the experimental program on Mueller Matrix Spectroscopy directed by one of the authors (AHC).

3.1 Ethylene Oxide, Isotopomer of Ammonia (NHDT) and Methyl Thiirane

In order to assess the feasibility of theoretically predicting VCD spectra, as a reasonable first step it seemed appropriate to carry out calculations on molecules for which experimental and theoretical results already existed in the literature. First, ethylene oxide has been previously investigated by Amos et. al. (14) The geometry used by these investigators, given in Figure 4, was used here also and in one study 4-31G level calculations were performed using the CADPAC package. The atomic polar tensor and the atomic axial tensor, given by equations (4) and (5), agree with Table 3 of reference (14). The calculated frequencies and rotational strengths determined in a related study at the 3-21 G level are reported in Table 2.

Next, the isotopomer of ammonia (NHDT) was studied with the following geometric parameters: nitrogen - hydrogen distance (r_{NH}) = 1.011609 Å and hydrogen - nitrogen - hydrogen bond angle (θ_{HNN}) = 106.697815 a.u. Calculations were carried out at both the 3-21G and 4-31 G levels. The results are reported in Tables 3 and 4. The energies and dipole moments agree with quantities reported in reference (15). An important point to note here is that, for the most part, signs of transitions with high rotational strengths remain unchanged with basis set and even though the magnitude of the rotational strength changes for transitions of high magnitude, the magnitude remains high as the basis set is changed. For transitions of low magnitude the sign of the rotational strength can change as the basis set is changed. The frequencies calculated here have not been scaled or adjusted in any way at this time. This scaling of the force field is discussed as an important point for further work in section IV.

Then, attention was turned to methyl thiirane. Experimental and theoretical work was carried out by Polavarapu et. al. (17) and calculations were carried out by Dothe, Lowe and Alper (18,19). A comparison of results are given Table 5 with the 3-21G optimized geometry given in Table 6 and shown in Figure 5. Calculated frequencies are qualitatively similar to the 6-31G level calculation. A comparison of the rotational strengths with the rotational strengths determined by a scaled quantum mechanical(SQM) force field determined from a 6-31G* level calculation shows the agreement is

reasonable as to the relative magnitude and the sign. For the most part a transition corresponding to a high rotational strength at the 3-21G level of calculation agrees in sign with the more extensive scaled 6-31G* level of calculation.

3.2 Hydrogen Peroxide and Hydrogen Persulfide

As a next step in study a few small molecules were investigated. Hydrogen peroxide (HOOH) and hydrogen persulfide (HSSH) were investigated with the results reported in Tables 7-10 and Figures 6 and 7. At this time we are not aware of any experimental VCD spectra of HOOH or HSSH.

3.3 Sugar-like Molecules and Sugars

Next, attention was focussed on molecules that are sugar-like in terms of functional groups and sugars with three to six carbon atoms (19). The sugar-like molecules studied were isotopomers of hydroxyacetaldehyde, hydroxymethyl ether, ethylene glycol and dimethyl ether. Calculated frequencies, rotational strengths and optimized geometries are reported in Tables 11-18 and the optimized geometries are shown in Figures 8-11. In addition optimized structures for the three carbon atom sugar D-glyceraldehyde and the four carbon atom sugar D-erythrose have been obtained and are reported in Tables 19 and 20 and shown in Figures 12 and 13. The frequencies and the rotational strengths have not been reported because of the unavailability at this time of the CRAY-XMP computer on which the CADPAC computer program is run. The VCD parameters will be determined once CRAY-XMP computer becomes available so as to complete this phase of the project. In addition optimization of the geometry of the four carbon atom sugar D-threose is nearing completion and once this is completed the VCD spectral parameters will be determined from CADPAC.

3.4 Discussion

Through examination of given spectral ranges, it is possible to scan each table of frequencies and rotational strengths to predict at which frequency a maximum rotational strength should be observed. The quality of the results can be seen by focusing on the VCD results found for methyl thiirane which are summarized in Table 5. The key points to note are the following:

1. The calculation is sensitive, because of the nature of the quantum mechanical operators involved - namely the angular momentum, to the choice of origin of the coordinate system. Comparisons in the literature at present find better agreement with the choice of origin as the center of mass of the molecule. Very key to the calculation is the level of the calculation. As mentioned our calculations are carried out at the 3-21G level, the origin chosen was the center of mass.
2. The inaccuracies that result will be manifest in
 - force field generated
 - atomic polar tensor
 - atomic axial tensor

Our calculation of rotational strengths, compared to 6-31G level calculations, for the majority of fundamental frequencies predict transitions of high rotational strengths and the correct sign. Transitions with low strengths can have their magnitude and sign changed as one uses another basis set.

The calculations on ammonia agree with results reported in the literature as to the values of the atomic polar and atomic axial tensors and the rotational strengths. The frequencies determined in the references (15,16) have been arrived at by an empirical force field (Duncan-Mills). As has been mentioned the ab initio unscaled frequencies will be somewhat high compared to experimental frequencies.

4. FUTURE DIRECTIONS

The following work is suggested to continue the project toward the generation of a library of theoretically predicted VCD spectra:

1. Complete work on the four carbon atom sugars
2. Label the modes of vibration for all molecules that were studied and compare with experimental data or other calculations where available.
3. Carry out studies of sugars with five carbon atoms and six carbon atoms. Investigate sugars with ring structures, such as glucose.
4. Investigate the sensitivity of the 3-21G level of calculation to carrying out optimizations with greater tolerances for gradient convergence, such as 10^{-6} . The tolerance used for the gradient convergence for the studies reported here was 10^{-4} .
5. Investigate larger basis set calculations, such as 6-31G or 6-31G*, using the 3-21G optimized structures as starting geometries.
6. Investigate the use of scaled force field and their effects on calculated frequencies, atomic polar tensors and atomic axial tensors and their subsequent effect on rotational strengths.

In order to obtain quantitative accuracy in the prediction of the VCD spectrum of a molecule, some form of scaling appears to be needed. However, if the main intent of the calculations is to predict the transitions of high rotational strength and their correct signs then 3-21G seems to be an adequate level to do the calculations at based on the small set of molecules that have been studied up to this point in time.

5. SUMMARY

We have undertaken the generation of a library of theoretically predicted VCD spectra. The approach involves the use of Stephens' theoretical formulation of the rotational strength and the use of Gaussian calculations at the 3-21G level. The results on molecules studied up to this point indicate that for transitions corresponding to high rotational strengths the signs remain insensitive to the basis set level used; in addition the magnitude of the rotational strength of a transition is sensitive to the basis set level that is used but a transition of high rotational strength at one level of calculation will tend also to be high at another level of calculation. It should be emphasized that the key assumptions being used are:

1. use of Stephens' theoretical formulation

2. use of Gaussian 3-21G level of calculation

The level of calculation affects the frequencies, atomic polar tensor, atomic axial tensor, and thereby the rotational strength.

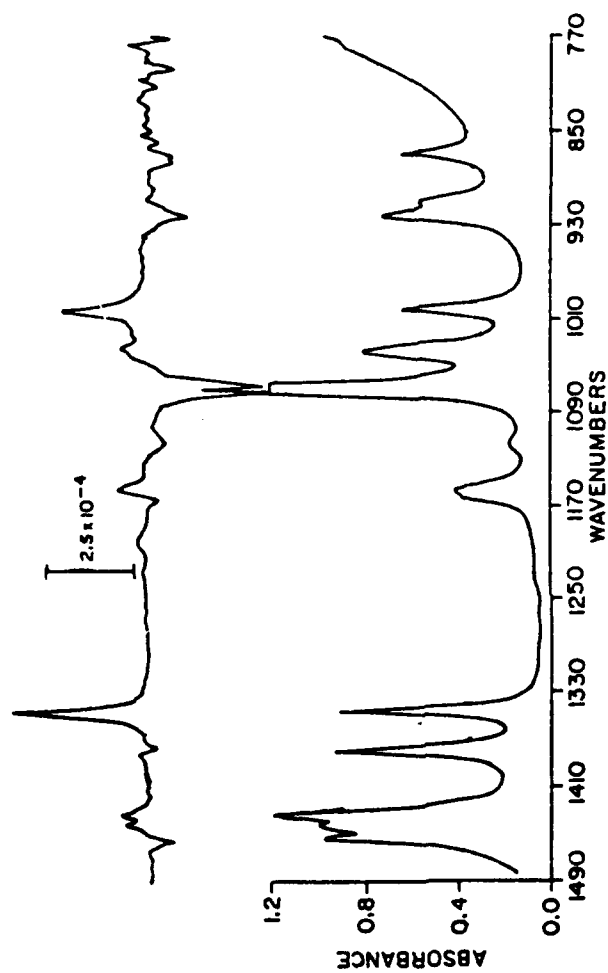


Figure 1. Infrared absorption (bottom) and circular dichroism(top) of (R)-methylothiirane in the 1500-800 cm^{-1} region. The measurements were made with neat liquid in a variable path length cell using minimum path lengths 15 μ . This figure is taken from the reference P. L. Polavarapu et al., J. Chem. Phys. 86, 1140-46 (1987)."

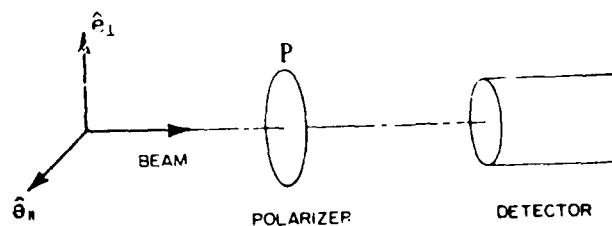


Figure 2. Schematic diagram of an experiment in which radiation is transmitted through an optical element. The detector measures the irradiance of the beam transmitted by the polarizer P [see C. F. Bohren and D. F. Huffman, "Absorption and Scattering of Light by Small Particles", Wiley-Interscience, New York (1983), Chapter 2].

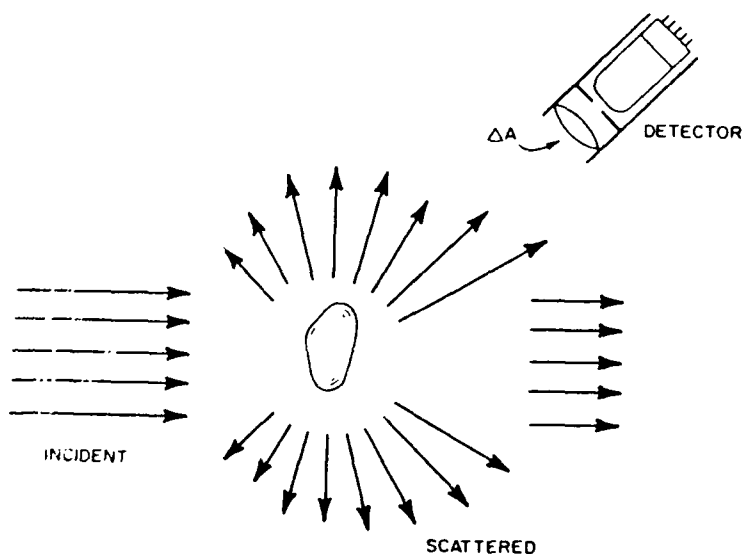


Figure 3. Schematic diagram of an experiment in which radiation is scattered by a single particle or collection of particles. The collimated detector responds only to scattered light [see C. F. Bohren and D. F. Huffman, "Absorption and Scattering of Light by Small Particles", Wiley-Interscience, New York (1983), Chapter 3].

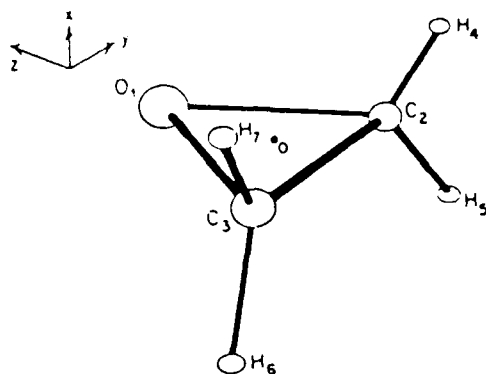


Figure 4. The geometry of ethylene oxide.

The internal coordinates are $r_{\text{CH}} = 1.086 \text{ \AA}$, $r_{\text{OC}} = 1.462 \text{ \AA}$, $r_{\text{CO}} = 1.428 \text{ \AA}$, $\theta_{\text{OCH}} = 114.5^\circ$, $\theta_{\text{OCH}} = 119.1^\circ$, $\theta_{\text{HCH}} = 116.9^\circ$. The Cartesian axes are as shown; z is the C_2 molecular axis and the ring is in the yz plane. The origin o is on the C_2 axis, 0.853 \AA from the oxygen atom. O is at the center of mass [see R. D. Amos, N. C. Handy, K. J. Jalkanen and P. J. Stephens, Chem. Phys. Letters 133 , 21-26 (1987)].

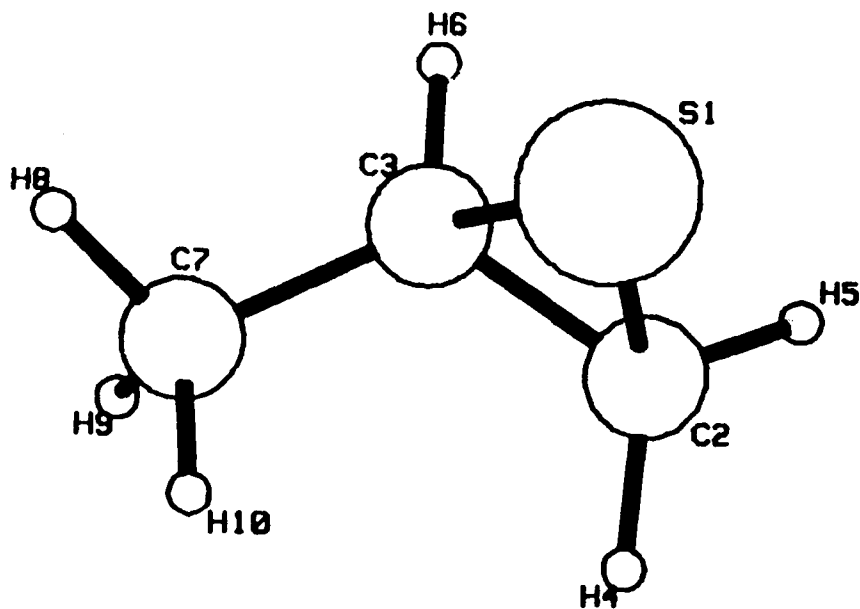


Figure 5. Optimized geometry(3-21G level) of methyl thiirane ($\text{C}_3\text{H}_6\text{S}$)

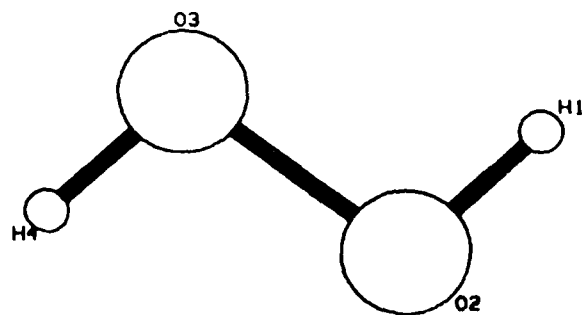


Figure 6. Optimized geometry(3-21G level) of hydrogen peroxide (H_2O_2)

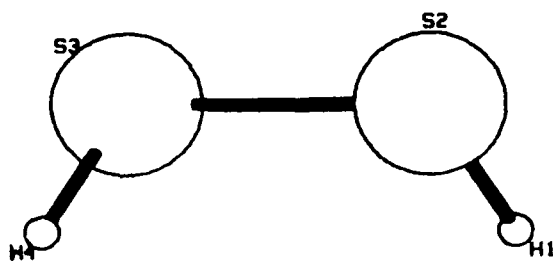


Figure 7. Optimized geometry(3-21G level) of hydrogen persulfide (H_2S_2)

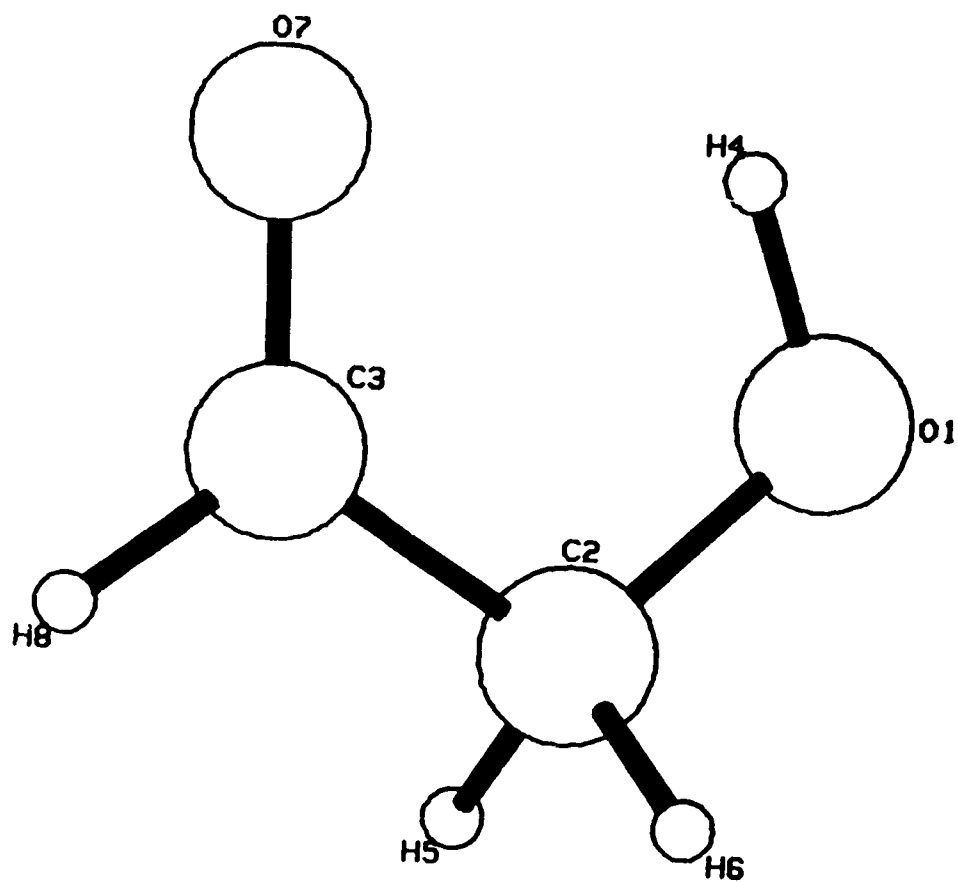


Figure 8. Optimized geometry(3-21G level) of hydroxyacetaldehyde (C₂H₄O₂)

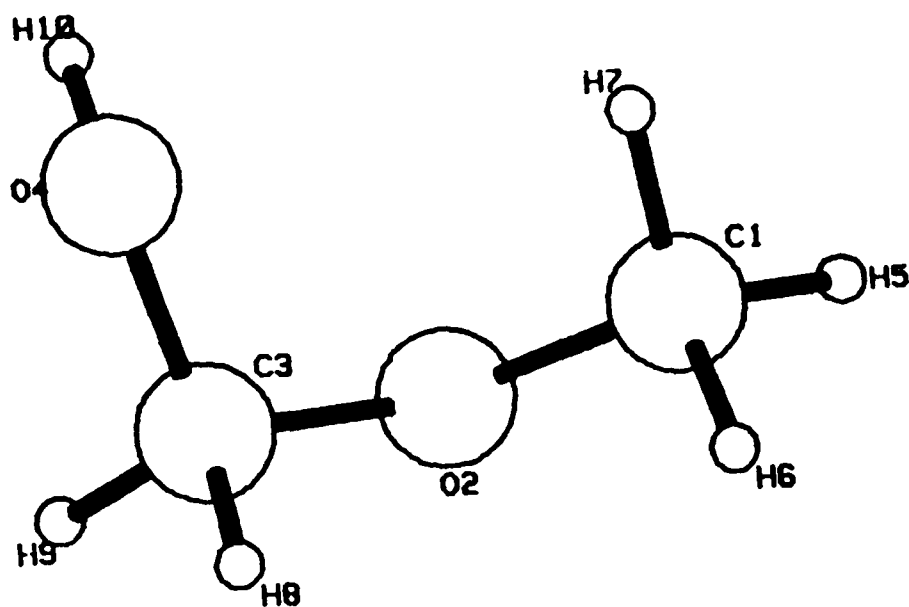


Figure 9. Optimized geometry(3-21G level) of hydroxymethyl ether ($C_2H_6O_2$)

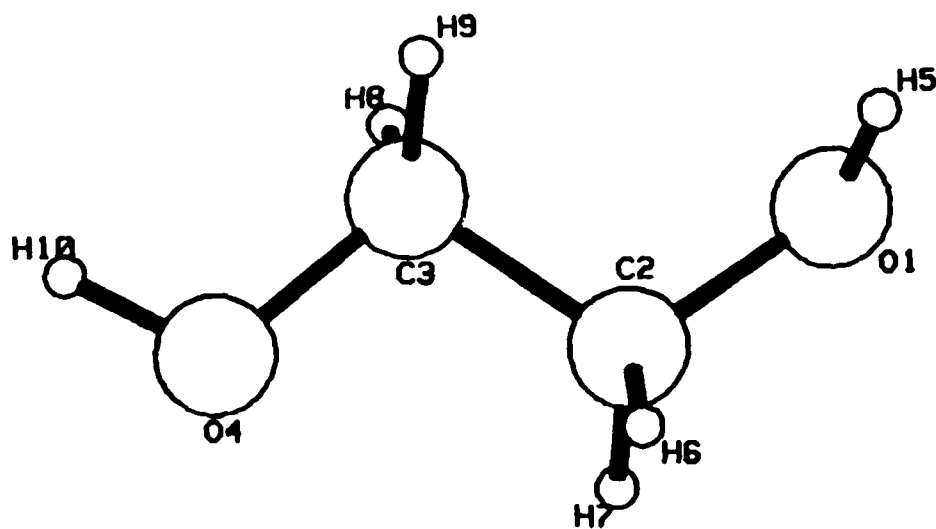


Figure 10. Optimized geometry(3-21G level) of ethylene glycol ($C_2H_6O_2$)

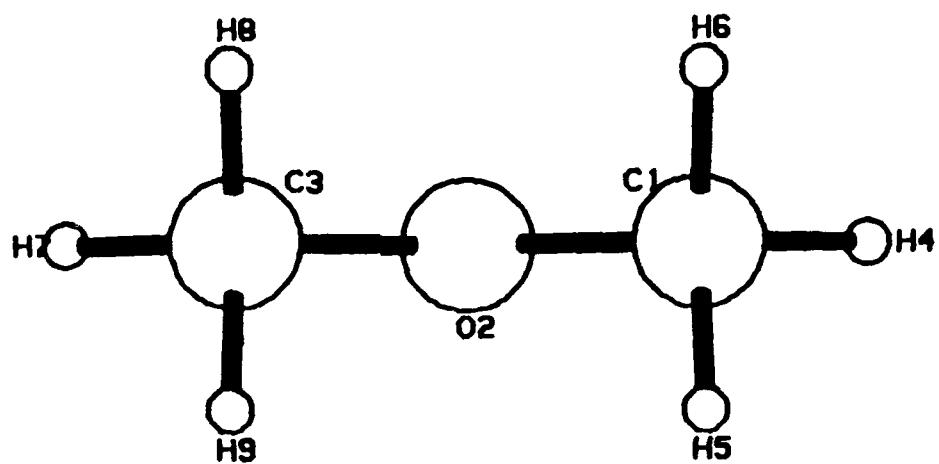


Figure 11. Optimized geometry(3-21G level) of dimethyl ether (C₂H₆O)

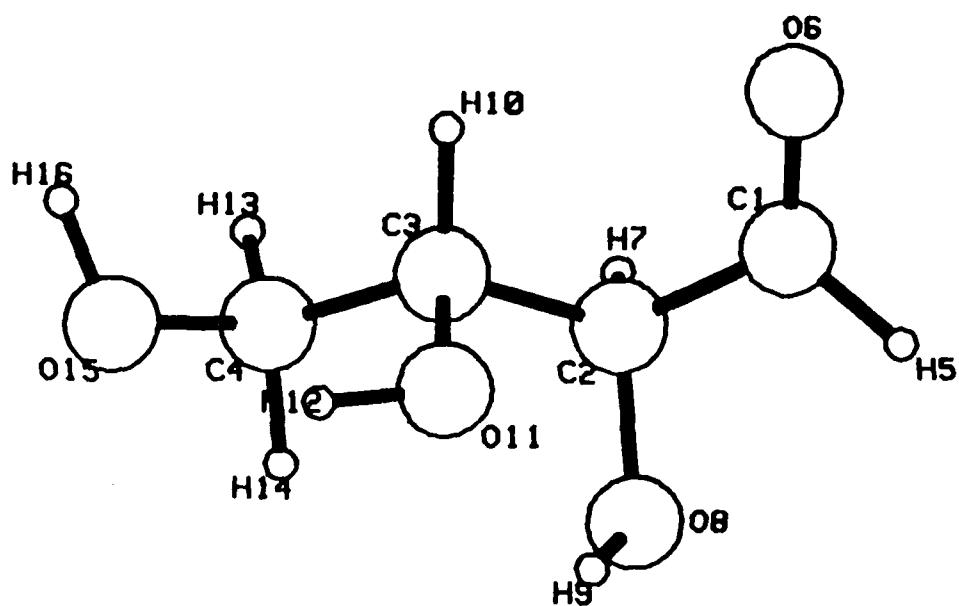


Figure 13. Optimized geometry(3-21G level) of D-erythrose ($C_4H_8O_4$)

TABLE 1. Stokes Parameters for Polarized Light

<i>Linearly Polarized</i>				
0° ↔	90° ↓	+45° ↗	-45° ↘	γ
$\begin{pmatrix} 1 \\ 1 \\ 0 \\ 0 \end{pmatrix}$	$\begin{pmatrix} 1 \\ -1 \\ 0 \\ 0 \end{pmatrix}$	$\begin{pmatrix} 1 \\ 0 \\ 1 \\ 0 \end{pmatrix}$	$\begin{pmatrix} 1 \\ 0 \\ -1 \\ 0 \end{pmatrix}$	$\begin{pmatrix} 1 \\ \cos 2\gamma \\ \sin 2\gamma \\ 0 \end{pmatrix}$
<i>Circularly Polarized</i>				
	Right ⊙		Left ⊙	
	$\begin{pmatrix} 1 \\ 0 \\ 0 \\ 1 \end{pmatrix}$		$\begin{pmatrix} 1 \\ 0 \\ 0 \\ -1 \end{pmatrix}$	

TABLE 2. Calculated Wavenumbers $\tilde{\nu}$ and Rotational Strengths R for Ethylene Oxide (C₂H₄O) Based on Geometry shown in Figure 1.*

$\tilde{\nu}$ (cm ⁻¹)	R (x 10 ⁻⁴⁴ esu ² cm ²)
935.32	0.
939.52	0.000834
972.85	-0.000744
1190.51	0.
1233.74	0.001365
1310.86	0.
1313.93	-0.000218
1316.13	-0.000482
1406.52	0.
1674.80	0.
1706.69	0.
3156.53	0.
3171.58	0.
3248.94	0.
3266.77	0.

TABLE 3. Calculated Wavenumbers $\tilde{\nu}$ and Rotational Strengths R for the Isotopomer of Ammonia (NHDT) Based on Geometry ($r_{\text{NH}} = 1.011609 \text{ \AA}$, $\theta_{\text{HNN}} = 106.697815^\circ$) used by Jalkanen et. al., J. Chem. Phys. 142, 153(1987).

[The total energy $E_{\text{tot}} = -55.870479593 \text{ a.u.}$ and dipole moment = -0.855236 a.u.]. The Frequencies and Rotational Strengths Obtained by Jalkanen et. al., Based on a Duncan-Mills Force Field, are Included in Parentheses. Calculations are Done at the 3-21 G Level.

$\tilde{\nu} (\text{cm}^{-1})$	R ($\times 10^{-44} \text{ esu}^2\text{cm}^2$)
976.57(826.62)	-10.620(-9.29)
1352.70(1195.18)	19.432(18.99)
1676.81(1483.96)	-10.510(-9.70)
2224.70(2176.42)	0.090(0.00)
2662.35(2600.81)	0.787(0.43)
3647.66(3561.51)	-0.540(-0.19)

TABLE 4. Calculated Wavenumbers $\tilde{\nu}$ and Rotational Strengths R for the Isotopomer of Ammonia (NHDT) Based on Geometry ($r_{\text{NH}} = 1.011609 \text{ \AA}$, $\theta_{\text{HNN}} = 106.697815^\circ$) used by Jalkanen et. al., J. Chem. Phys. 142, 153(1987).

[The total energy $E_{\text{tot}} = -56.102481085 \text{ a.u.}$ and dipole moment = -0.904429 a.u.]. The frequencies and rotational strengths obtained by Jalkanen et. al., based on a Duncan-Mills force field, are included in parentheses. Calculations are done at the 4-31 G level.

$\tilde{\nu} (\text{cm}^{-1})$	R ($\times 10^{-44} \text{ esu}^2\text{cm}^2$)
1022.67(826.62)	-12.327(-9.70)
1357.39(1195.18)	21.868(19.86)
1677.65(1483.96)	-11.501(-10.24)
2219.84(2176.42)	0.890(0.58)
2658.03(2600.81)	-0.319(-0.18)
3641.00(3561.51)	-0.060(-0.06)

TABLE 5. A Comparison of Wavenumbers ν and Rotational Strengths R for Methyl Thiirane

ν (cm ⁻¹)			R (x 10 ⁻⁴⁴ esu ² cm ²)	
Ref. a	Ref. b	This work	Ref. a	This work
220	-	238.23	7.9	2.196
301	305	312.65	-0.82	-8.078
377	391	427.46	-1.7	3.568
585	592	538.24	-14.4	-9.637
628	644	602.72	22.1	11.396
861	885	925.39	-36.8	-14.875
896	957	943.69	54.2	21.076
908	1011	1043.99	-21.6	-19.318
992	1098	1108.86	73.2	21.285
1043	1151	1172.80	40.9	52.519
1078	1197	1207.44	-173.7	-98.711
1151	1224	1248.83	5.2	-1.470
1169	1268	1324.05	35.9	-11.557
1341	1446	1506.98	15.0	46.377
1387	1543	1586.01	0.85	-2.889
1434	1578	1624.52	17.7	4.697
1446	1605	1655.00	-5.4	8.194
1452	1614	1664.66	-3.5	-14.743
2861	3089	3205.64	0.59	-1.512
2919	3146	3264.62	-2.0	7.475
2943	3168	3272.64	9.4	-6.989
3018	3235	3344.02	3.6	-0.427
3040	3276	3378.51	-10.5	6.182
3098	3317	3444.78	3.2	0.016

Ref. a = H. Dothe, M.A.Lowe and J.S.Alper, J. Phys. Chem. **92**, 6246-49 (1988). These authors have used the scaled quantum mechanical (SQM) force field to obtain vibrational frequencies and the transformation matrix from cartesian coordinates to normal coordinates that is needed in the VCD calculation of rotational strengths. Original calculations were carried out at the 6-31 G* level.

Ref. b = P. L. Polavarapu et. al., J. Chem. Phys. **86**, 1140-46 (1987). These authors carry out ab initio calculations at the 6-31 G level.

This work = Calculations carried out at the 3-21 G level.

TABLE 6. Optimized Geometry for Methyl Thiirane
(C₂SH₃CH₃) Based on 3-21G Level of Calculation
[The total energy = -511.9828737 a.u. and the dipole moment =
3.01852 D.]

geometrical coordinate	value of geometrical coordinate
r(S ₁ -C ₂)	1.9345 Å
r(C ₂ -C ₃)	1.4636 Å
r(C ₂ -H ₄)	1.0708 Å
r(C ₂ -H ₅)	1.0700 Å
r(C ₃ -H ₆)	1.0715 Å
r(C ₃ -C ₇)	1.5082 Å
r(C ₇ -H ₈)	1.0835 Å
φ(C ₃ -C ₂ -S ₁)	67.754 °
φ(H ₄ -C ₂ -C ₃)	118.408 °
φ(H ₅ -C ₂ -C ₃)	119.065 °
φ(H ₆ -C ₃ -C ₂)	116.724 °
φ(C ₇ -C ₃ -C ₂)	119.880 °
φ(H ₈ -C ₇ -C ₃)	110.412 °
τ(H ₄ -C ₂ -C ₃ -S ₁)	104.653 °
τ(H ₅ -C ₂ -C ₃ -S ₁)	-103.887 °
τ(H ₆ -C ₃ -C ₂ -S ₁)	103.046 °
τ(C ₇ -C ₃ -C ₂ -S ₁)	-107.542 °
τ(H ₈ -C ₇ -C ₃ -S ₁)	76.805 °
τ(H ₅ -C ₇ -C ₃ -S ₁)	-163.473 °
τ(H ₁₀ -C ₇ -C ₃ -S ₁)	-42.922 °

TABLE 7. Calculated Wavenumbers $\tilde{\nu}$ and Rotational Strengths R for Hydrogen Peroxide (HOOH) Based on 3-21G Level Optimized Geometry

mode	$\tilde{\nu}$ (cm ⁻¹)	R (x 10 ⁻⁴⁴ esu ² cm ²)
torsion	87.10	-6.117
	1167.99	-0.174
	1278.05	-0.506
	1644.43	0.094
	3328.40	-1.236
	3845.25	1.888

TABLE 8. Optimized Geometry for Hydrogen Peroxide (HOOH) Based on 3-21G Level of Calculation

geometrical coordinate	value of geometrical coordinate
r(O-H)	0.9703 Å
r(O-O)	1.4731 Å
ϕ (H-O-O)	99.451 °
τ (H-O-O-H)	178.595 °

TABLE 9. Calculated Wavenumbers $\tilde{\nu}$ and Rotational Strengths R for Hydrogen Persulfide (HSSH) Based on 3-21G Level Optimized Geometry

mode	$\tilde{\nu}$ (cm ⁻¹)	R ($\times 10^{-44}$ esu ² cm ²)
torsion	337.34	-159.66
	462.28	-0.808
	897.81	30.828
	912.98	-29.138
	2632.15	-6.583
	2633.82	0.224

TABLE 10. Optimized Geometry for Hydrogen Persulfide (HSSH) Based on 3-21G Level of Calculation

geometrical coordinate	value of geometrical coordinate
r(S-H)	1.3514 Å
r(S-S)	2.2638 Å
ϕ (H-S-S)	96.707 °
τ (H-S-S-H)	93.830 °

TABLE 11. Calculated Wavenumbers ν and Rotational Strengths R for the Isotopomer of Hydroxyacetaldehyde (CHDOH-CHO) Based on 3-21G Level Optimized Geometry

$\tilde{\nu}$ (cm ⁻¹)	R (x 10 ⁻⁴⁴ esu ² cm ²)
174.52	-1.5369
317.00	-0.8014
397.23	-9.3339
755.26	67.952
808.78	-28.285
882.65	-81.512
1004.03	27.579
1166.53	74.788
1222.99	-57.161
1389.71	0.3105
1487.43	43.712
1519.10	-42.697
1541.64	-5.9977
1906.71	10.576
2358.19	24.699
3206.11	-63.704
3223.24	39.647
3828.49	1.2695

TABLE 12. Optimized Geometry for the Isotopomer of Hydroxyacetaldehyde
(CHDOH-CHO) Based on 3-21G Level of Calculation.
[The total energy = -226.484421186 a.u. and the dipole moment =
2.9617 D.]

geometrical coordinate	value of geometrical coordinate
$r(O_1-C_2)$	1.4255 A
$r(C_2-C_3)$	1.5094 A
$r(O_1-H_4)$	0.9701 A
$r(C_2-H_5)$	1.0849 A
$r(C_2-H_6)$	1.0849 A
$r(C_3-O_7)$	1.2103 A
$r(C_3-H_8)$	1.0826 A
$\phi(C_3-C_2-O_1)$	110.420 °
$\phi(H_4-O_1-C_2)$	108.551 °
$\phi(H_5-C_2-O_1)$	110.663 °
$\phi(H_6-C_2-O_1)$	110.669 °
$\phi(O_7-C_3-C_2)$	121.590 °
$\phi(H_8-C_3-C_2)$	116.115 °
$\tau(H_4-C_2-O_1-C_3)$	-0.025 °
$\tau(H_5-C_2-O_1-H_4)$	120.293 °
$\tau(H_6-C_2-O_1-H_4)$	-120.360 °
$\tau(O_7-C_3-C_2-O_1)$	0.003 °
$\tau(H_8-C_3-C_2-O_1)$	179.997 °

TABLE 13. Calculated Wavenumbers ν and Rotational Strengths R for the Isotopomer of Hydroxymethyl ether ($\text{CH}_3\text{-O-CHDOH}$) Based on 3-21G Level Optimized Geometry

ν (cm^{-1})	R ($\times 10^{-44}$ esu $^2\text{cm}^2$)
150.63	25.440
197.25	-3.754
136.10	17.703
419.20	-33.412
618.97	17.865
924.28	19.796
991.27	74.355
1072.03	22.944
1150.26	-106.04
1224.07	38.492
1268.74	18.074
1313.02	20.976
1411.83	-50.363
1524.23	6.133
1551.44	-63.669
1625.46	8.489
1671.00	-6.482
1698.14	8.946
2398.46	-10.482
3209.41	8.844
3263.13	5.903
3271.06	-31.401
3285.84	4.546
3867.18	24.137

TABLE 14. Optimized Geometry for the Isotopomer of Hydroxymethyl ether
(CH₃-O-CHDOH) Based on 3-21G Level of Calculation.
[The total energy = -227.661102 a.u. and the dipole moment = 0.37208
D.]

geometrical coordinate	value of geometrical coordinate
r(C ₁ -O ₂)	1.4418 Å
r(O ₂ -C ₃)	1.4143 Å
r(O ₃ -C ₄)	1.4210 Å
r(O ₁ -C ₅)	1.0814 Å
r(O ₄ -C ₁₀)	0.9671 Å
∠(C ₃ -O ₂ -C ₁)	114.688 °
∠(O ₄ -C ₃ -O ₂)	112.470 °
∠(H ₅ -C ₁ -O ₂)	106.572 °
∠(H ₆ -C ₁ -O ₂)	110.816 °
∠(H ₇ -C ₁ -O ₂)	110.830 °
∠(H ₈ -C ₃ -O ₂)	111.513 °
∠(H ₉ -C ₃ -O ₂)	105.479 °
∠(H ₁₀ -O ₄ -C ₃)	110.488 °
∠(O ₄ -C ₃ -O ₂ -C ₁)	62.680 °
∠(H ₅ -C ₁ -O ₂ -C ₃)	-178.097 °
∠(H ₆ -C ₁ -O ₂ -C ₃)	62.801 °
∠(H ₇ -C ₁ -O ₂ -C ₃)	-58.252 °
∠(H ₈ -C ₃ -O ₂ -C ₁)	-55.079 °
∠(H ₉ -C ₃ -O ₂ -C ₁)	-174.840 °
∠(H ₁₀ -O ₄ -C ₃ -O ₂)	60.925 °

TABLE 15. Calculated Wavenumbers ν and Rotational Strengths R for the Isotopomer of Ethylene Glycol (CHDOH-CH₂OH) Based on 3-21G Level Optimized Geometry

ν (cm ⁻¹)	R (x 10 ⁻⁴⁴ esu ² cm ²)
145.07	13.598
275.29	220.23
287.60	140.72
294.46	-384.63
488.68	6.512
810.61	-9.441
979.33	24.161
1043.30	26.607
1128.76	4.467
1144.91	-36.410
1232.74	29.689
1323.41	-12.872
1335.22	-3.809
1397.95	-28.120
1489.16	31.741
1533.26	-24.860
1581.46	-3.362
1704.85	1.119
2396.71	-6.257
3212.47	4.063
3234.02	51.990
3258.77	-55.673
3872.00	6.592
3877.91	-3.438

TABLE 16. Optimized Geometry for the Isotopomer of Ethylene Glycol
(CHDOH-CH₂OH) Based on 3-21G Level of Calculation.
[The total energy = -227.6518901 a.u. and the dipole moment =
2.56172 D.]

geometrical coordinate	value of geometrical coordinate
$r(O_1-C_2)$	1.440 A
$r(C_2-C_3)$	1.521 A
$r(C_3-O_4)$	1.440 A
$r(O_1-H_5)$	0.966 A
$r(C_2-H_6)$	1.082 A
$\phi(C_3-C_2-O_1)$	110.279 °
$\phi(O_4-C_3-C_2)$	105.448 °
$\phi(H_5-O_1-C_2)$	110.994 °
$\phi(H_6-C_2-C_3)$	109.407 °
$\phi(H_7-C_2-C_3)$	109.407 °
$\phi(H_8-C_2-C_3)$	109.407 °
$\phi(H_9-C_2-C_3)$	109.407 °
$\phi(H_{10}-O_4-C_3)$	110.994 °
$\pi(O_4-C_3-C_2-O_1)$	178.917 °
$\pi(H_5-O_1-C_2-C_3)$	78.201 °
$\pi(H_6-C_2-C_3-O_4)$	-56.813 °
$\pi(H_7-C_2-C_3-O_4)$	61.786 °
$\pi(H_8-C_3-C_2-O_1)$	57.886 °
$\pi(H_9-C_3-C_2-O_1)$	-60.910 °
$\pi(H_{10}-O_4-C_3-C_2)$	-176.349 °

TABLE 17. Calculated Wavenumbers ν and Rotational Strengths R for
the Isotopomer of Dimethyl Ether (CHDT-O-CH₃) Based on 3-21G
Level Optimized Geometry

ν (cm ⁻¹)	R (x 10 ⁻⁴⁴ esu ² cm ²)
165.27	-5.2052
258.97	-7.8217
393.57	7.6908
883.63	-3.7270
956.41	-11.465
1055.51	9.7607
1141.22	0.4384
1236.85	-5.4182
1280.68	-0.2552
1305.47	-2.9711
1447.48	26.488
1486.33	-19.965
1635.26	1.1278
1678.55	1.0211
1690.78	0.6431
1989.75	13.079
2360.74	-14.611
3181.62	0.2114
3231.41	0.1558
3238.94	-1.1410
3252.97	0.2455

TABLE 18. Optimized Geometry for the Isotopomer of Dimethyl Ether
(CHDT-O-CH₃) Based on 3-21G Level of Calculation.
[The total energy = -153.212180696 a.u.ole moment =
1.8925 D.]

geometrical coordinate	value of geometrical coordinate
$r(C_1-O_2)$	1.4324 Å
$r(O_2-C_3)$	1.4324 Å
$r(C_1-H_4)$	1.0840 Å
$r(C_1-H_5)$	1.0840 Å
$r(C_1-H_6)$	1.0840 Å
$r(C_3-H_7)$	1.0840 Å
$r(C_3-H_8)$	1.0840 Å
$r(C_3-H_9)$	1.0840 Å
$\phi(C_3-O_2-C_1)$	113.190 °
$\phi(H_4-C_1-O_2)$	110.001 °
$\phi(H_5-C_1-O_2)$	110.001 °
$\phi(H_6-C_1-O_2)$	110.001 °
$\phi(H_7-C_3-O_2)$	110.005 °
$\phi(H_8-C_3-O_2)$	110.005 °
$\phi(H_9-C_3-O_2)$	110.005 °
$\tau(H_4-C_1-O_2-C_3)$	-179.981 °
$\tau(H_5-C_1-O_2-C_3)$	59.921 °
$\tau(H_6-C_1-O_2-C_3)$	-59.884 °
$\tau(H_7-C_3-O_2-O_2)$	179.993 °
$\tau(H_8-C_3-O_2-C_1)$	59.897 °
$\tau(H_9-C_3-O_2-C_1)$	-59.910 °

TABLE 19. Optimized Geometry for the Isotopomer of D-Glyceraldehyde
(CHO-HCOH-CH₂OH) Based on 3-21G Level of Calculation.
[The total energy = -339.7416503 a.u. and the dipole moment = 3.4498
D.]

geometrical coordinate	value of geometrical coordinate
$r(C_1-C_2)$	1.5103 Å
$r(C_2-C_3)$	1.5286 Å
$r(C_1-H_4)$	1.0820 Å
$r(C_1-O_5)$	1.2077 Å
$r(C_2-H_6)$	1.0810 Å
$r(C_2-O_7)$	1.4439 Å
$r(C_7-H_9)$	0.9655 Å
$r(C_8-H_{10})$	1.0827 Å
$r(C_8-H_{11})$	1.0779 Å
$r(C_8-O_{11})$	1.4344 Å
$r(O_{11}-H_{12})$	0.9681 Å
$\phi(C_2-C_3-C_1)$	109.217 °
$\phi(H_4-C_1-C_2)$	113.171 °
$\phi(O_5-C_1-C_2)$	123.679 °
$\phi(H_6-C_2-C_1)$	110.335 °
$\phi(O_7-C_2-C_1)$	109.089 °
$\phi(H_8-O_7-C_2)$	112.428 °
$\phi(H_9-C_8-C_2)$	108.690 °
$\phi(H_{10}-C_8-C_2)$	110.831 °
$\phi(O_{11}-C_8-C_2)$	108.504 °
$\phi(H_{12}-O_{11}-C_8)$	107.757 °
$\pi(H_4-C_1-C_2-C_3)$	78.170 °
$\pi(O_5-C_1-C_2-C_3)$	-99.786 °
$\pi(H_6-C_2-C_1-H_4)$	200.808 °
$\pi(O_7-C_2-C_1-H_4)$	-33.907 °
$\pi(H_8-O_7-C_2-C_1)$	-73.590 °
$\pi(H_9-C_8-C_2-C_1)$	-181.367 °
$\pi(H_{10}-C_8-C_2-C_1)$	58.027 °
$\pi(O_{11}-C_8-C_2-C_1)$	-59.027 °
$\pi(H_{12}-O_{11}-C_8-C_2)$	-59.687 °

TABLE 20. Optimized Geometry for D-Erythrose (CHO-HCOH-HCOH-CH₂OH) Based on 3-21G Level of Calculation.

[The total energy = -453.008065 a.u. and the dipole moment = 3.00471 D.]

geometrical coordinate	value of geometrical coordinate
r(C ₁ -C ₂)	1.5156 A
r(C ₂ -C ₃)	1.5215 A
r(C ₃ -C ₄)	1.5226 A
r(C ₁ -H ₅)	1.0839 A
r(C ₁ -O ₆)	1.2074 A
r(C ₂ -H ₇)	1.0827 A
r(C ₂ -O ₈)	1.4282 A
r(O ₆ -H ₉)	0.9714 A
r(C ₃ -H ₁₀)	1.0807 A
r(C ₃ -O ₁₁)	1.4438 A
r(O ₁₁ -H ₁₂)	0.9698 A
r(C ₄ -H ₁₃)	1.0821 A
r(C ₄ -H ₁₄)	1.0771 A
r(C ₄ -O ₁₅)	1.4509 A
r(O ₁₅ -H ₁₆)	0.9663 A
∠(C ₃ -C ₂ -C ₁)	110.196 °
∠(C ₄ -C ₃ -C ₂)	112.421 °
∠(H ₅ -C ₁ -C ₂)	113.564 °
∠(O ₆ -C ₁ -C ₂)	123.165 °
∠(H ₇ -C ₂ -C ₃)	110.846 °
∠(O ₈ -C ₂ -C ₃)	109.653 °
∠(H ₉ -O ₆ -C ₁)	106.172 °
∠(H ₁₀ -C ₃ -C ₂)	109.921 °
∠(O ₁₁ -C ₃ -C ₂)	104.007 °
∠(H ₁₂ -O ₁₁ -C ₃)	107.836 °
∠(H ₁₃ -C ₄ -C ₃)	111.752 °
∠(O ₁₅ -C ₄ -C ₃)	108.925 °
∠(O ₁₅ -C ₄ -C ₂)	107.857 °
∠(H ₁₆ -O ₁₅ -C ₄)	111.275 °
∠(C ₄ -C ₃ -C ₂ -C ₁)	171.623 °
∠(H ₅ -C ₁ -C ₂ -C ₃)	137.045 °
∠(O ₆ -C ₁ -C ₂ -C ₃)	-43.836 °
∠(H ₇ -C ₂ -C ₃ -C ₄)	51.303 °
∠(O ₈ -C ₂ -C ₃ -C ₄)	-67.691 °
∠(H ₉ -O ₆ -C ₁ -C ₂)	81.697 °
∠(H ₁₀ -C ₃ -C ₂ -C ₁)	46.310 °
∠(O ₁₁ -C ₃ -C ₂ -C ₁)	-72.685 °
∠(H ₁₂ -O ₁₁ -C ₃ -C ₂)	203.203 °

$\tau(\text{H}_{15}-\text{C}_4-\text{C}_3-\text{C}_2)$	-73.658 °
$\tau(\text{H}_{14}-\text{C}_4-\text{C}_3-\text{C}_2)$	47.640 °
$\tau(\text{O}_{15}-\text{C}_4-\text{C}_3-\text{C}_2)$	-197.374 °
$\tau(\text{H}_{16}-\text{O}_{15}-\text{C}_4-\text{C}_{12})$	86.553 °

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